Environmental impact of the excess electricity conversion into methanol

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ARTICLE INFO

ABSTRACT

In this work, the impact on the environment of a renewable methanol production in combination with a wastewater treatment plant (WWTP) was analysed. Carbon dioxide from biogas and hydrogen from water electrolysis were used as resources for methanol synthesis. Additionally, it was decided to use the available excess of electricity and it was prepared for a small city in North-West of Germany (Emden) to have a realistic scenario. As a consequence, methanol plant was simulated with the use of ASPEN Plus software in order to calculate the mass balance and energy requirement. Subsequently a comparative life cycle assessment (cradle-to-gate) was conducted in order to compare renewable methanol with conventional process and also with methanol produced from biomass. In order to evaluate possible impact on the environment, 11 common impact categories were selected. Results showed that enough excess electricity was already available to utilize the whole CO_2 from WWTP in Emden. Subsequently it was found that the production of renewable methanol, without emissions related to windmill construction, has much lower impact on the environment than conventional production according to all impact categories. Furthermore, the combination of power-to-methanol plant with WWTP allowed utilization of the biogenic carbon dioxide and application of the produced via electrolysis oxygen. Therefore, thanks to substitution of air with produced oxygen, a reduction in electricity consumption for the aeration system could be possible. However, taking into account the emissions related to wind electricity, renewable methanol would cause lower emissions according to 5 impact categories (acidification potential, climate change, ozone layer depletion, photochemical oxidation, and primary energy demand from non-renewable resources) than natural gas or biomass based methanol.

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1. Introduction

The further expansion of wind power (WP) in Germany is noticeable, because alone in 2016, 1288 new windmills were constructed, with net installed electricity capacity of over 4259 MW. Furthermore, new plants built in 2016 account for 4.7% of all plants (27 270) in operation on the 31st of December 2016 in Germany, which together have the net installed electricity capacity of over 45,910 MW electric power. Taking under consideration that German wind energy's market is already very mature, such a market growth is significant (Deutsche WindGuard GmbH, 2017).

As a consequence, days like Sunday, the 8th of Mai 2016, when 87.6% of energy demand was covered with renewable energy (RE), are predicted to occur more often (WeltN24 GmbH, 2016). Furthermore, in Denmark already on Thursday, the 9th of July 2015 the electricity produced from windmills exceeded the domestic electricity demand (116%) (Neslen, 2015) and in Scotland also, the windmills covered the whole demand on Sunday, the 7th of August 2016 (The Guardian, 2016). However, further expansion of WP and other RE lead also to a situation when the grid is overloaded. Occasionally windmills or photovoltaic-plants (PV-plant) in Germany need to be switch off due to the grid overload, still obtaining reimbursement. Therefore initiatives like "switch over despite switch off" (German "*Umschalten statt Abschalten*") from German Federal Association of Wind Energy are promoting alternative

usage of the excess electricity (German Federal Association of Wind Energy, 2015).

Currently there are many alternative storage options of the excess electricity, like e.g. production of hydrogen (Uusitalo et al., 2017), or alternative usages like e.g. production of ammonia (ISPT, 2017). Furthermore, even some of the possible energy storage solutions are actually utilizing carbon dioxide like conversion to methane, methanol (Uusitalo et al., 2017) or formic acid (Moret et al., 2014), hence allowing energy storage for a later usage. On the other hand, looking at the current findings about diesel emissions and its impact on premature deaths (Anenberg et al., 2017), conversion of excess of electricity into fuel, which is less toxic (Olah et al., 2009), would be very convenient. Moreover, its energy density at ambient conditions equals to 4.4 kWh/l (Chemie.de Information Service GmbH, 2017) and in contrast to hydrogen, which energy density at ambient conditions equals to 3 Wh/l and at 700 bar equals to 1.4 kWh/l (PLANET- Planungsgruppe Energie und Technik GbR, 2013), makes methanol an interesting alternative as an energy storage medium. As a consequence, methanol is an interesting option and could be applied as a fuel for vehicles (Bicer und Dincer, 2017a; Hao et al., 2017; Li et al., 2010; Shen et al., 2012; Trudewind et al., 2014a, 2014b; Zhen und Wang, 2015) aircrafts (Bicer und Dincer, 2017b) rail (Dincer und Zamfirescu, 2016) and ships (Brynolf et al., 2014; Strazza et al., 2010). According to IHS (Information Handling Services Markit), already in 2014 7000 thousand metric tons of methanol were directly used as a fuel out of 63,965 thousand metric tons produced worldwide (IHS Markit, 2017). Additionally, methanol is used for production of formaldehyde, MTBE (methyl tert-butyl ether), acetic acid (Olah et al., 2009; Van-Dal und Bouallou, 2013) and MTO (methanol to olefins, like ethylene and propylene), and is also possible application of it at the wastewater treatment plant for the denitrification process (Methanol Institute, 2017).

In order to ensure reduction in the environmental burden of e.g. new fuels before introducing them on a large scale, life cycle assessment (LCA) is a widely recognized method used for evaluation of possible environmental benefits over e.g. conventional production. Trudewind et al. prepared a life-cycle assessment and well-to-wheel analysis indicating that the photocatalytically produced methane has a lower ecological impact than photocatalytically produced methanol (Trudewind et al., 2014a, 2014b). Subsequently, an assessment of the methanol chemical synthesis from carbon dioxide and hydrogen together with comparison to conventional methanol production was conducted by Hoppe et al., where 3 parameters (global warming potential (GWI), total material requirement, raw material input) and the CO_2-source were analysed (Hoppe und Bringezu, 2016; Hoppe et al., 2017). In their system the German electricity mix was applied for production of methanol and wind energy was used for electrolysis. They included hydrogen production but produced oxygen was not further considered. One of the key findings is, that CO_2 from direct air capture is significantly increasing the environmental impact in means of all the three parameters analysed, due to excessive heat and electricity demand. Pérez-Fortes et al. analysed a net reduction of CO_2 emissions and a cost of methanol production. They indicated that a capital cost of methanol plant synthesized from hydrogen and captured carbon dioxide, not including electrolyser and carbon capture unit, is lower than for conventional plants. But the cost of resources (H_2 and CO_2) does not allow the project to be financially attractive, as long as the price of hydrogen would decrease almost 2.5 times or the price of methanol would be two times more expensive. Nevertheless, they also found that a very small reduction of carbon dioxide emissions could be achieved, but it needs to be kept in mind that they are operating the plant with electricity from

a conventional pulverised coal plant as a worst case scenario (Pérez-Fortes et al., 2016). Matzen and Demirel prepared a fully comparative LCA (cradle-to-grave) of a very big scale methanol (96.7 tons per day) and dimethyl ether (68.5 tons per day) plants from renewable hydrogen and captured carbon dioxide. They included the production of CO_2 via ethanol plant, hence biomass growth, harvesting etc. was included in their system boundary along with construction of windmills. Authors also used the renewable electricity for operating the facility and for electrolysis. According to the five impact categories (Global Warming Potential, Acidification Potential, Photochemical Oxidation Formation, Particulate Matter Formation, Human Toxicity) analysed, renewable methanol production has lower impact on the environment compared to dimethyl ether or the conventional processes. However, according to the authors, methanol has a higher impact on the environment than dimethyl ether during combustion, Yet it is noteworthy that the largest environmental impact still was found to be related to the fuel production stage for both fuels (Matzen und Demirel, 2016). Finally Uusitalo et al., (2017) used the excess of electricity for production of hydrogen, methane and methanol and looked at the greenhouse gas (GHG) emission. Authors stated that the highest reduction on GHG was achieved with hydrogen, but all three options indicated high GHG reduction potential if applied in transportation (Uusitalo et al., 2017).

Consequently authors identify a need for a fully comparative methanol life cycle (cradle-to-gate) assessment, where production of the renewable methanol from the excess electricity will be compared to conventional process and to methanol from biomass. The comparison will be conducted according to 11 impact categories, in order to identify eventual impact of the methanol production. Finally, in this concept the power-to-methanol plant will be located at the wastewater treatment plant, which allows application of the produced via electrolysis oxygen, what is not considered in other LCA analysis. The whole methanol plant is simulated with ASPEN Plus® and for life cycle assessment GABI® software is employed.

2. Material and methods

2.1. Methanol production

The methanol production process is a catalytic conversion of carbon monoxide and carbon dioxide with hydrogen at elevated temperature (250 °C) and pressure (50 bar) in presence of e.g. CuO/ZnO/Al$_2$O$_3$ catalyst (Sahki et al., 2011). Obtaining those conditions would allow both exothermic reactions (eq. 1 and eq. 2) to take place (Van-Dal und Bouallou, 2013):

$$CO + 2H_2 \leftrightarrow CH_3OH \ \ \Delta H = -128 \frac{kJ}{mol} \ (298\,K)$$
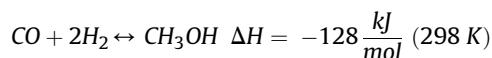
Equation 1 Methanol synthesis from carbon monoxide (Van-Dal und Bouallou, 2013)

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \ \ \ \Delta H = -87 \frac{kJ}{mol} \ (298\,K)$$
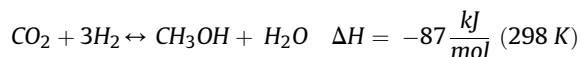
Equation 2 Methanol synthesis from carbon dioxide (Van-Dal und Bouallou, 2013).

The required gas mixture, so a synthesis gas, is obtained from natural gas for the conventional methanol production (Van-Dal und Bouallou, 2013). But the synthesis gas can also be obtained from the biomass (Cheng, 2009) or as the resources could directly serve the captured carbon dioxide and derived via electrolysis hydrogen (eq. 2) (Van-Dal und Bouallou, 2013).

2.2. Conventional methanol production

The conventional production of methanol from natural gas is already presented in the ecoinvent 3.3 database and only the electricity source is modified to German grid mix. In the system boundary (Fig. 1) included is the gas conditioning, hence desulphurisation and steam reforming, before methanol catalytic synthesis and distillation. The desulphurisation is necessary to achieve the concentration below 280 μg H_2S/m^3, in order to avoid deactivation of the nickel catalyst. According to the process description, the removed sulphur is realised in form of SO_2, causing additional impact on the environment. The required catalysts for desulphurisation ($NiO/MoO_3/Al_2O_3$), steam reforming (NiO/Al_2O_3) and methanol synthesis ($CuO/ZnO/Al_2O_3$) are included in the evaluation. Furthermore, according to the description of the database, the required amount of catalyst per process was assumed to be 133 mg per 1 kg of methanol produced. The used catalyst was not treated as a waste instead recycling was applied, but it was not included in the system boundary. Since the produced vapours are containing carbon monoxide, hydrogen and trace concentration of methanol, this stream is burned in the furnace, causing additional NOx emissions considered in the LCA (Althaus et al., 2007).

2.3. Biomass to methanol production

Methanol produced from biomass is also considered for this comparative assessment. The system boundary as presented on Fig. 2 was included in the ecoinvent 3.3. database and only the electricity source is modified to German grid mix. Due to the similarity of methanol production from natural gas and biomass, significant part is based on the conventional production, like e.g. water usage, furnace emissions catalyst amounts, wastewater etc. However, since part of the syngas is utilized for covering plants' needs, e.g. the supply of electricity and heat for the whole process and related emission are adjusted to consumption of syngas produced from biomass (Jungbluth et al., 2007).

2.4. Simulation of the methanol production

The methanol plant was simulated in ASPEN Plus V9® (Fig. 3) in accordance to Van-Dal and Bouallou (Van-Dal und Bouallou, 2013). They used kinetic model of Vanden Bussche and Froment (Vanden Bussche und Froment, 1996) with readjusted parameters of Mignard and Pritchard (Mignard und Pritchard, 2008). However, as stated by Van-Dal and Bouallou direct implementation of this kinetic model in Aspen Plus was not possible, therefore authors rearranged it in order to use the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model, as shown in Eqs. 3, Eqs. 4 and Eqs. 5, where parameters are used from Table 1. Here pressure is given in Pa and temperature in K. Authors also compared the results of the rearranged model to the model of Vanden Bussche and Froment indicating a very good fit. However, by-productslike
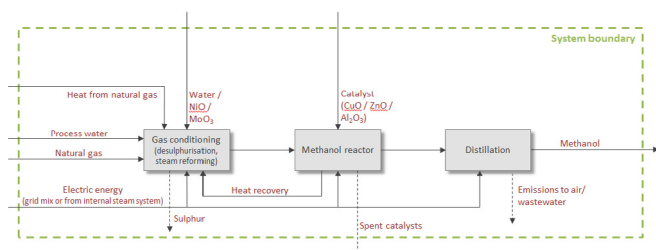

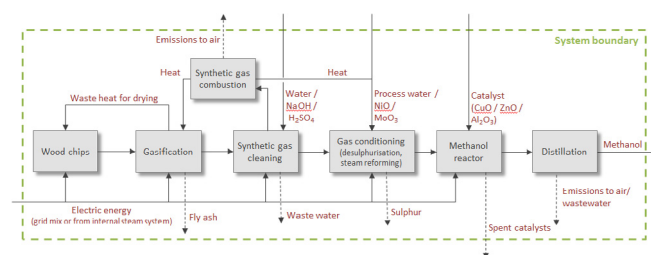**Fig. 1.** System boundary of methanol production from natural gas.

Fig. 2. System boundary of methanol production from biomass derived synthetic gas.
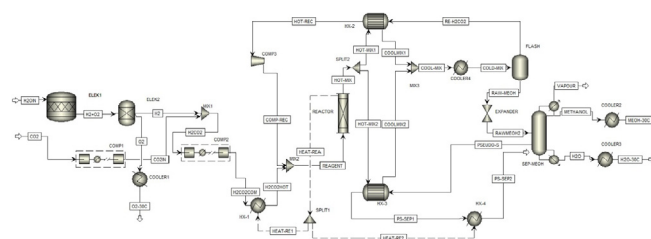

Fig. 3. Methanol plant simulated in ASPEN Plus V9®.

Table 1
Parameters values for the kinetic model [B given in J/mol] (Van-Dal und Bouallou, 2013).

k_1	A_1	1.07
	B_1	40 000
k_2	A_2	3453.38
	B_2	–
k_3	A_3	0.499
	B_3	17 197
k_4	A_4	$6.62 \cdot 10^{-11}$
	B_4	124 119
k_5	A_5	$1.22 \cdot 10^{10}$
	B_5	−98 084
k_6	A_6	17.55
	B_6	−2249.8
k_7	A_7	0.1310
	B_7	−7023.5

hydrocarbons, higher alcohols or methyl formatewere not considered by the authors (Van-Dal and Bouallou, 2013) and were omitted in the simulation, but the future research will concentrate on this aspect.

$$r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} - k_6 P_{H_2O} P_{CH_3OH} P_{H_2}^{-2}}{\left(1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}\right)^3} \left[\frac{kmol}{kg_{cat}s}\right]$$

Equation 3 Methanol Synthesis (Van-Dal und Bouallou, 2013)

$$r_{RWGS} = \frac{k_5 P_{CO_2} - k_7 P_{H_2O} P_{CO} P_{H_2}^{-1}}{1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}} \left[\frac{kmol}{kg_{cat}s}\right]$$

Equation 4 Reverse water gas shift reaction (Van-Dal und Bouallou, 2013)

$$ln\, k_i = A_i + \frac{B_i}{T}$$

Equation 5 Temperature dependence of the parameters (Van-Dal und Bouallou, 2013).

In the model (Fig. 3) four stage compression (COMP1 and COMP2) of the gases was applied, as proposed in the literature (Van-Dal und Bouallou, 2013). Between every compression, apart

from the last stage, gases are cooled since it is thermodynamics favourable. In addition to that, energy consumption was optimized with use of Pinch method (Kemp, 2007). As a consequence, the hot gas phase (HOT-MIX) coming from reactor was split (SPLIT2), so 94.2% (HOT-MIX1) is used for re-heating the recycled stream (RE-H2CO2) via heat exchanger (HX-2). Left stream (HOT-MIX2) is used to partially heat the reboiler of the separator represented by a pseudo stream (PSEUDO-S). Moreover, despite application of heat exchangers for the hot mixture of methanol/carbon dioxide/ hydrogen (HOT-MIX), the cooler stream (COOL-MIX) still needs to be cooled to 313.15 K (COOLER4) before the separation in flash will be possible. On the other side, because methanol synthesis reaction is exothermic, the excess of heat (HEAT-REA) is used for heating the fresh CO_2/H_2 mixture coming to reactor (H2CO2COM) via heat exchanger (HX-1) and also for the final preparation of the separator (PS-SEP1) via (HX-4). In contrast to work of Van-Dal and Bouallou (Van-Dal und Bouallou, 2013), the oxygen was utilized in this system hence cooling (COOLER1) it to 313.15 K, which is necessary before application at WWTP, was included in the calculation. Furthermore, produced methanol and water are also cooled (respectively COOLER2 and COOLER3) to 313.15 K. As the methanol reactor (REACTOR), as proposed in the literature (Van-Dal und Bouallou, 2013), was chosen a plug flow reactor *(RPLUG)* with packed bed, but with co-current thermal fluid. The size of reactor was chosen to consist of 30 tubes, each 1 m long and with diameter of 0,025 m. The further specification of the plant can be found in the literature (Van-Dal und Bouallou, 2013).

2.5. Life cycle assessment

The life cycle assessment has been prepared in dependence on the ISO 14040 (EN ISO 14040:2006) and ISO 14044 (EN ISO 14044:2006) standards. The software used for LCA preparation was GaBi® ts equipped with ecoinvent 3.3 database, however the energy balance and mass balance were prepared with ASPEN Plus V9® simulation software. Despite that, literature data were also used which are explained in section 2.6 and summarised as a Fig. 4. In this research, it was decided to compare conventional production of methanol from natural gas and from biomass, with renewable methanol produced from the excess electricity. Consequently, the functional unit was chosen to be 1 kg of methanol. It was decided that the application of methanol is not considered in this article, hence a cradle-to-gate assessment (Fig. 5) was prepared. As resources for the renewable methanol, hydrogen produced via electrolysis and captured carbon dioxide were chosen. Moreover, the plant was theoretically located in Emden (North-West Germany) at the wastewater treatment plant (WWTP), where produced biogas served as a carbon dioxide source.
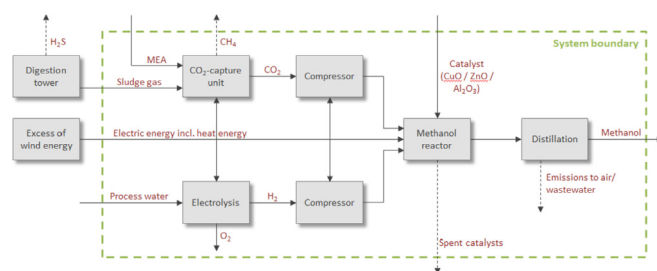

Fig. 5. System boundary of the methanol production from captured carbon dioxide and excess of wind energy.
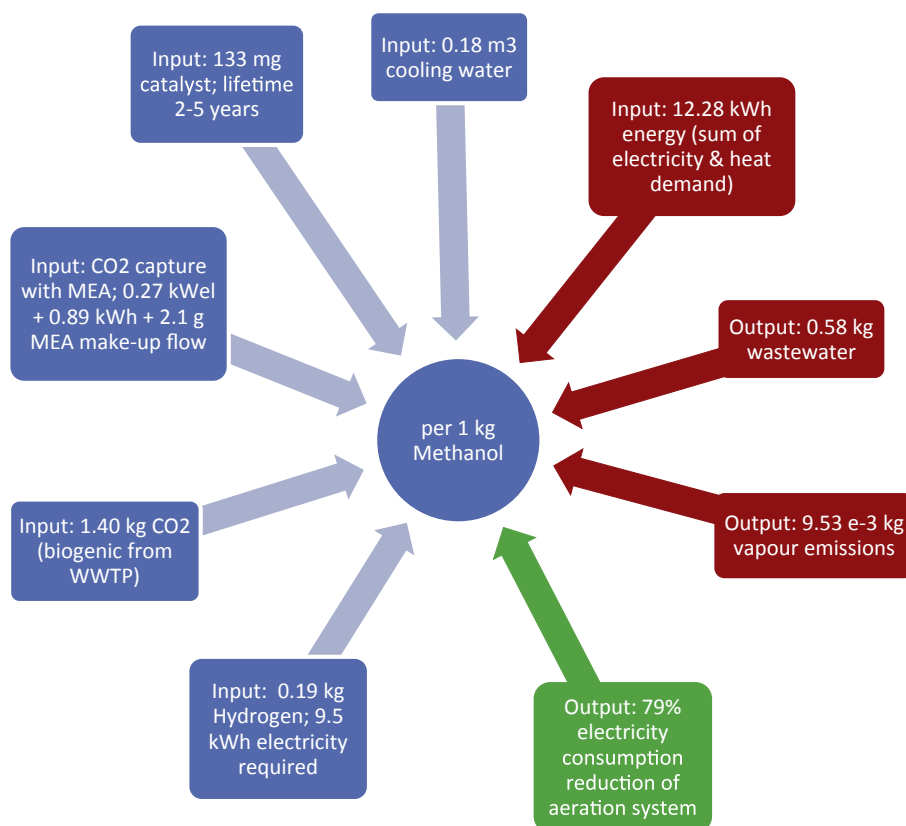

Fig. 4. Summary of the inventory data and assumptions (Sternberg und Bardow, 2015; Uusitalo et al., 2017; Koornneef et al., 2008; Abu-Zahra et al., 2007; Althaus et al., 2007).

2.6. Inventory data and assumptions

2.6.1. Hydrogen

The first renewable resource is obtained via electrolysis process, where water is converted into hydrogen and oxygen with the use of electricity. There are three available electrolyser types on the market, which include alkaline electrolysis cell (AEC), high temperature electrolysis, and proton exchange membrane electrolyser (PEM) (Uusitalo et al., 2017). Because in this research the excess electricity is used as energy source, electrolyser with a very rapid response time capable for grid balancing is necessary, therefore PEM electrolyser was chosen (Bourne 25.04.2017; Sternberg und Bardow, 2015). According to the literature, the electricity consumption required to produce 18–22 kg of hydrogen equal to 1 MWh (Sternberg und Bardow, 2015).

2.6.2. Carbon dioxide

The wastewater treatment plant in Emden is operating for 75000 inhabitants and its 'maximum capacity is 90000 inhabitants. The averaged flow is between 11000 and 12000 m^3/d and during the raining days it is almost doubled. The source of carbon dioxide is a biogas produced via anaerobic digestion of the excess of sludge coming from wastewater treatment plant. According to the data received from WWTP in Emden, average biogas production in 2016 equalled to 1434 m^3/d, from which 33.5 vol % was carbon dioxide. Therefore, it was calculated that 951 kg CO_2 per day are available for the methanol plant and this value was used as a starting point for simulation. Moreover, the present CO_2 is actually an unwanted by-product and since the CO_2 capture improved the heating value of the biogas, it was decided to use CO_2 as a waste product without upstream chain.

Furthermore, produced biogas was already utilized via Combined Heat and Power (CHP) unit, hence desulphurisation and drying unit was already installed at the plant. Therefore, in this assessment only the emissions related to carbon capture were included. But, the biogas methane obtained after upgrading is not included in the system boundary and in this analysis (Fig. 5).

For carbon dioxide capture different techniques are available, including adsorption, water scrubbing and membrane separation (Deublein und Steinhauser, 2011). However, taking into account maturity of amine scrubbing method with Monoethanolamine (MEA) (Rochelle, 2009) and availability of data for the analysis (Abu-Zahra et al., 2007; Jadhav et al., 2014; Uusitalo et al., 2017), this method was chosen for carbon dioxide capture. But it needs to be taken into account, that the desorption is achieved at elevated temperature and due to MEA degradation a make-up flow is necessary, as stated by Uusitalo et al., (2017). According to the literature (Abu-Zahra et al., 2007; Koornneef et al., 2008; Uusitalo et al., 2017), carbon dioxide capture with use of MEA require 0.27 kW electricity and 0.89 kW heat per 1 kg of methanol produced. In addition to that, it is necessary to include a make-up flow of 2.1 g MEA per 1 kg of Methanol as indicated in the literature (Uusitalo et al., 2017). The emissions related to MEA production are also included in the analysis.

The WWTP is a carbon dioxide source independent from fossil fuels, hence it allows a longer and sustainable perspective of serving as a CO_2 source than e.g. coal power plant. It was assumed, that the CO_2 has been removed from the atmosphere in upstream plant growth processes and is therefore set as biogenic. Furthermore, since in the selected system boundaries the use of the methanol is excluded, the methanol behaves as a short-term CO_2 storage.

2.6.3. Catalyst

For the renewable methanol the same catalyst (64% CuO/24%

ZnO/balance Al_2O_3) as for other process is applied. The required amount equals to 133 mg per 1 kg methanol and the lifetime of a catalyst is between 2 and 5 years (Althaus et al., 2007).

2.6.4. Wastewater

The produced water (Table 2) coming from the bottom stage of the distillation unit is treated as a wastewater due to its contamination with methanol and it is included in the LCA calculation, as it is also considered for the conventional production.

2.6.5. Electricity

As stated in the introduction, due to the grid overloading, occasionally windmills or photovoltaic-plants in Germany need to be switched off (German Federal Association of Wind Energy, 2015). Therefore it was proposed to utilize this excess electricity for a methanol production instead. So it was applied for acquisition of the resources along with operating the whole methanol plant. Moreover, it was decided to prepare two scenarios, where in the first one evaluated the impact of windmill's upstream chain. In the second scenario, it is assumed that the windmills due to grid overloading would be switched off, therefore the wind upstream chain is not considered. The electricity and heating requirements for production of 1 kg methanol is presented in Table 2. Furthermore, utilization of the whole CO_2 (347 tons/a) available from WWTP would require 2.86 GWh/a and would allow production of 233 tons of methanol per year (Fig. 6). According to the data available from public utility company in Emden (Stadtwerke Emden, 2016), the excess electricity in years 2014 and 2015 was already

Table 2
Mass balance of the simulated methanol plant.

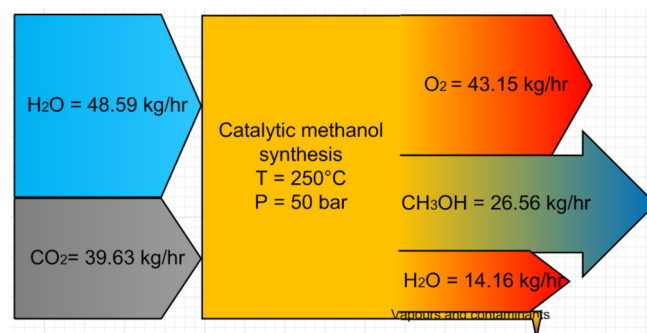|		Stream	Mass [kg]
Input		H_2O	1.83
		CO_2	1.49
Output	Main product (methanol)	H_2	$2.93 \cdot 10^{-6}$
		CO_2	$5.72 \cdot 10^{-3}$
		H_2O	$4.41 \cdot 10^{-2}$
		CH_3OH	1.00
		CO_2	$4.21 \cdot 10^{-6}$
	Product (water)	H_2	$2.88 \cdot 10^{-29}$
		CO_2	$1.60 \cdot 10^{-23}$
		H_2O	0.53
		CH_3OH	$5.56 \cdot 10^{-5}$
		CO_2	$8.29 \cdot 10^{-34}$
	Product (vapour)	H_2	$8.14 \cdot 10^{-5}$
		CO_2	$2.02 \cdot 10^{-3}$
		H_2O	$5.83 \cdot 10^{-6}$
		CH_3OH	$4.35 \cdot 10^{-4}$
		CO_2	$2.74 \cdot 10^{-5}$
	Product (oxygen)	O_2	1.62

Fig. 6. Summary of the simulated methanol plant's mass balance.

>5 GWh/a, theoretically allowing the utilization of the whole available from WWTP carbon dioxide.

2.6.6. Cooling

The cooling requirement of the simulated plant is summarised in Table 3. The necessary 0.176 m^3 cooling water for 1 kg methanol is included in the LCA calculation (Table 4).

2.6.7. Vapour emissions

Following the conventional process, a combustion in the furnace is required due to the composition of the vapour (Table 2) produced during the distillation process. This additional step caused emissions included in the LCA assessment.

2.6.8. Oxygen utilization

The wastewater treatment plant (WWTP) was chosen as a location for our plant not only because it delivers carbon dioxide, but because also here application of produced oxygen is possible. One of the processes of sewage treatment is aerobic biological treatment, where aeration is necessary in order to achieve the recommended concentration of 2 g O_2/m^3 necessary for optimal conversion of organic contaminants. Furthermore, following the literature, aeration system is responsible for 76.47% of the electricity consumption at the WWTP in Emden (Lindenthal et al., 2013). Moreover, as already proposed by Dohmann and Schröder, the oxygen produced via electrolysis could be used for the aeration system (Dohmann und Schröder, 2011). Hence it is here considered and for the calculation was used technical specification of the Lenntech BV turbine applied at WWTP for aeration, according to which 22 kg O_2/hr is delivered via 11 kW high speed turbine

Table 3
Summary of the duty and electricity balance from simulated methanol plant.

Process	Heating and Electricity	
Electrolyser	273	[kW]
Compressor 1	2.10	[kW]
Cooler1		[kW]
Compressor2	6.16	[kW]
Reactor		[kW]
Cooler4		[kW]
Separator	13.26	[kW]
Cooler2		[kW]
Cooler3		[kW]
Compressor3	0.72	[kW]
CO_2 separation with amines (Uusitalo et al., 2017)	30.70	[kW]
$\sum$ Total duty	325.94	[kW]
Energy required per 1 kg Methanol	12.27	[kWh/kg Methanol]
Yearly energy demand	2.86	[GWh/a]

Table 4
Summary of the cooling requirement for the simulated methanol plant.

Process	Cooling	
Compressor 1	1.53	[kW]
Cooler1	0.56	[kW]
Compressor2	6.42	[kW]
Reactor	12.90	[kW]
Cooler4	23.44	[kW]
Separator	19.91	[kW]
Cooler2	0.69	[kW]
Cooler3	1.77	[kW]
$\sum$ Cooling	67.22	[kW]
Water requirement	4681.34	[kg]
Water requirement per 1 kg methanol	176.27	[kg/kg Methanol]

(Lenntech BV, 2017). Due to the substitution of air with pure oxygen, the turbine is pumping almost 79% less gases into water in order to achieve the required concentration of 2 g O_2/m^3. The achieved reduction of "Germany-Electricity-Mix" consumption and related emissions were understood as credits in this study.

3. Results and discussion

3.1. Cradle-to-gate comparative assessment

For the LCIA 11 categories were analysed, from which 10 categories were in accordance to Reference Life Cycle Data System (ILCD). The additional 11th category was the *primary energy demand from non-renewable resources*. The analysed system was a production of renewable methanol from excess electricity (Fig. 4) with and without wind upstream chain. As reference systems the conventional production of a methanol from natural gas (Fig. 2) and from biomass based synthetic gas (Fig. 3) were used.

The first analysed impact category was the acidification potential (Fig. 7), according to which the highest impact could be caused by the methanol from biomass based synthetic gas (sg-MeOH). For 84% of this result (3.3e^{-03} kg SO_2-eq/kg methanol), synthetic gas upstream processes, so gasification, gas cleaning, gas conditioning and wood chips processing are responsible. The required electricity for methanol synthesis is responsible for 9% of the sg-MeOH's acidification potential. On the contrary the methanol from natural gas (ng-MeOH) has by 5e^{-04} [kg SO_2-eq/kg methanol] lower acidification potential, by which the major impact is ascribed to natural gas, gas conditioning and necessary resources for synthesis gas preparation (77%), along with required heat (12.5%). The emissions estimated for the renewable methanol (re-MeOH) with wind upstream chain and without assigned credits are still 1.7 times lower than of the sg-MeOH. In 72% this potential is caused by the emissions related to production and operation of the windmills and in 24% by the upstream chain of ultrapure water. The calculated emissions are lower than presented in the literature (Matzen und Demirel, 2016), because in this research the carbon dioxide upstream chain, like biomass cultivation, related emission from transportation and agriculture processes, was not relevant to the scenario with wastewater treatment plant. Moreover, the exclusion of wind upstream chain would over 6 times lower the emissions, when compared to biomass based methanol. For this scenario the production and utilization of the ultrapure water is responsible for 86.5% of the potential. For the additional 8% of the emissions, the application of MEA for carbon capture technique is responsible. Therefore further reduction could be achieved by application of an another method. Taking into account the credit from oxygen application, the impact of the wind upstream chain is not
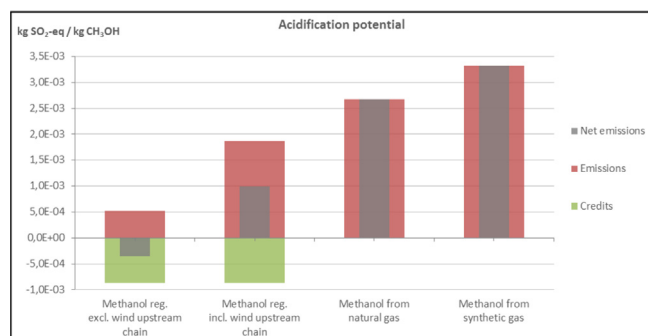

Fig. 7. Comparison of renewable methanol to conventional methanol in accordance to acidification potential.

recompensed, but if the windmill needs to be shut down and the oxygen utilization would be possible, then the emissions became actually negative (Fig. 7).

In the climate change impact category (Fig. 8), the credits for utilization of the biogenic CO_2 are assigned to renewable methanol (re-MeOH) and biomass based methanol (sg-MeOH). As a consequence, the emissions related to sg-MeOH could become 75% lower and would only be slightly higher than for natural gas based methanol (ng-MeOH), which is in line with Hoppe et al., (2017). After inclusion of the credits, 99% of the sg-MeOH's impact is caused by the methanol production, related emissions and required electricity. By the ng-MeOH the natural gas and its' preparation is responsible for 55% of the climate change impact category, 33% is assigned to the heat requirement, and 7.5% is caused by the electricity required for methanol production. The emissions of re-MeOH with wind upstream chain are by over a half lower than the emissions related to ng-MeOH. For this process again, utilization of wind energy and related construction (70%) and application of the ultrapure water (26%) are mostly responsible for this impact category. In contrast to work of (Matzen und Demirel, 2016), the CO_2 was treated as an unwanted derivative from the wastewater treatment plant, therefore the carbon dioxide upstream chain was not included and the lower emissions were calculated. However, taking under consideration credits for oxygen utilization at the WWTP and application of biogenic CO_2, the emissions would become negative. Exclusion of the wind upstream chain by re-MeOH lowers the related emissions and now the application and preparation of ultrapure water is responsible for 84.5% of the result. The carbon capture with MEA is responsible for 12.5% of the emissions related to climate change and then a substitution of this method could even further decrease the impact on the environment. However, according to Hoppe et al., application of the direct air capture technique could significantly increase environmental impact due to excessive heat and electricity demand (Hoppe et al., 2017). Furthermore, the emissions of both re-MeOH systems on the climate change are lower than the results presented in the literature for different sources of CO_2, like biogas plant or cement plant (Hoppe et al., 2017). However, it needs to be noticed that Hoppe et al. used German electricity mix for the processes apart from hydrogen production and they did not consider utilization of the oxygen. Moreover, the achieved results indicate lower impact on the environment than from the work of (Matzen und Demirel, 2016), because they included in their system boundary the whole cultivation and preparation chain of the biomass for ethanol production, which then served as a CO_2 source. Furthermore, the influence of using the biogenic CO_2 was neglected in this publication. For our case, a wastewater treatment plant served as a carbon dioxide source, hence no biomass cultivation was necessary to be analysed.

By the depletion of abiotic resources (Fig. 9) the wind upstream chain included for the renewable methanol (re-MeOH) caused the highest emissions (93%), which would lead to a much higher impact on the environment than of natural gas based or synthesis gas based methanol. Source of the higher emissions is the need for including e.g. copper, gold and cadmium, as well as the associated emissions during windmills construction. Without wind upstream chain, the major emissions are coming from processes related to ultrapure water utilization (53.5%), and carbon capture technique (10%). However, here also application of the copper oxide catalyst caused significant impact (36%). By the sg-MeOH not only the processes related to synthetic gas production (68.5%), but also application of the molybdenum (23%) for sulphur removal, are mostly responsible for the depletion of abiotic resources. Concerning the natural gas based methanol, the emissions could actually be 63.5% lower, if despite the molybdenum, another sulphur removal technique would be applied.

The fourth analysed impact category was eutrophication (Fig. 10), by which the highest forecasted impact is assigned to biomass based methanol (sg-MeOH). The emissions are caused by the production and preparation of synthesis gas (53%), electricity for methanol synthesis (31.5%), and application of the molybdenum for desulphurisation (6.5%). By the lower impact of natural gas based methanol (ng-MeOH), the resources preparation and natural gas utilization (42%) and electricity for methanol plant (21%) play a significant role. Additionally, the application of molybdenum for the gas conditioning is analysed separately and is identified to be responsible for 16% of the emissions. The inclusion of wind upstream chain for re-MeOH indicated a higher eutrophication potential as ng-MeOH, whereas wind upstream chain's share was calculated to be 67%. Additionally, the related emissions are in 29%
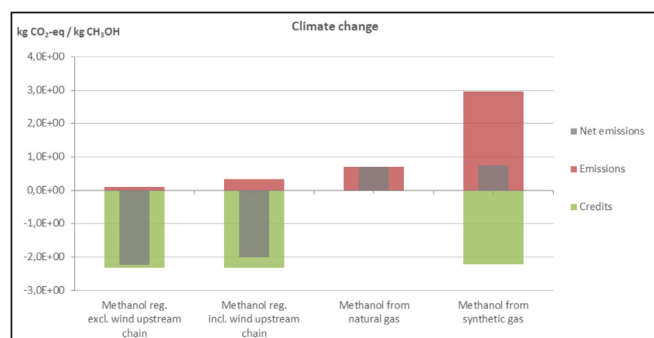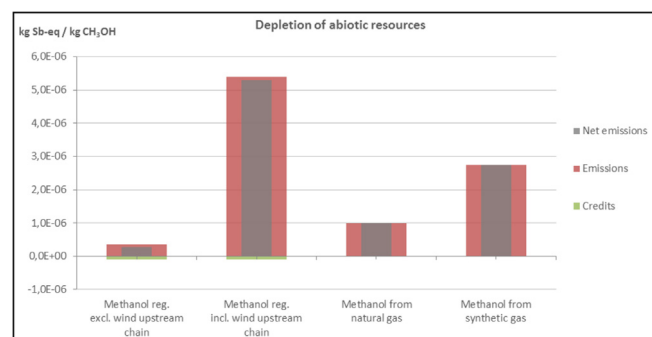
Fig. 9. Comparison of renewable methanol to conventional methanol in accordance to depletion of abiotic resources.

Fig. 8. Comparison of renewable methanol to conventional methanol in accordance to climate change.
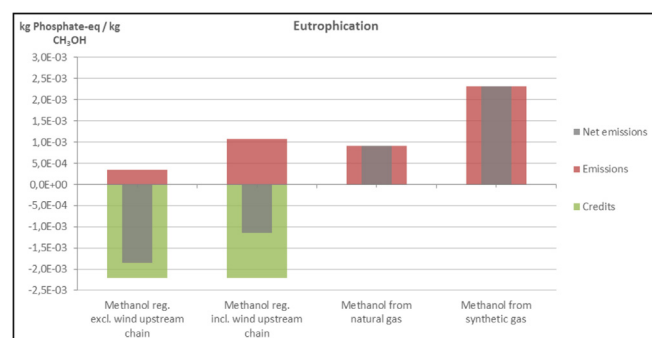
Fig. 10. Comparison of renewable methanol to conventional methanol in accordance to eutrophication potential.

cause also by the application of ultrapure water for the electrolysis and the share increased to 88% for renewable methanol without wind energy's impact. Emissions related to copper oxide catalyst (5.6%) and application of MEA for carbon capture (6.3%) are also noticeable.

The obvious highest impact on the freshwater aquatic ecotoxicity (Fig. 11) coming from the wind energy upstream chain (97%) cannot actually by balanced via assigned credits. Without considering it, the impact of renewable methanol is much lower than of other methanol processes, despite significant emissions related to from production of ultrapure water (66%), copper oxide catalyst (22.5%) and MEA-carbon capture technique (11%). For biomass based and natural gas based methanol processes is again preparation and application of resources (47% by sg-MeOH and 38% by ng-MeOH) responsible for most of the emissions. Additionally, electricity for methanol synthesis (32.5% by sg-MeOH and 17% by ng-MeOH) and application of molybdenum (10% by sg-MeOH and 20% by ng-MeOH) play also a significant role by emissions related to the freshwater aquatic ecotoxicity.

Responsible for almost 70% emissions related human toxicity category from renewable methanol without wind upstream chain (Fig. 12) is the application of primary amine (MEA), from which 98% is caused by the upstream chain of ethanolamine. Therefore a substitution of this amine or application of an alternative method would reduce the toxic emissions. The share of ultrapure water's upstream chain equals to 20.5% and also noticeable is the share of copper oxide catalyst (10%). Taking into account emissions related to wind energy, the emissions would increase almost 5 times for re-MeOH and would cause the highest emission among analysed systems. Despite that the calculated emissions are lower than in the literature (Matzen und Demirel, 2016) due to different system boundaries. The synthetic gas (65.5%) along with emissions related

to electricity for methanol production (over 16.5%) and molybdenum (11%) are responsible for the sg-MeOH's impact, which is again higher than of natural gas based methanol. For the ng-MeOH not only the natural gas and related process (42.5%) play a significant role, but also share in emissions of molybdenum (26%), electricity for methanol synthesis (10%), and the required heat (10.5%) is noticeable.

The seventh analysed impact category was marine aquatic ecotoxicity (Fig. 13), according to which emissions from re-MeOH without wind upstream chain would equal to 74 kg DCB-eq/kg Methanol. This high impact is affected in 69% by the ultrapure water upstream chain and in 19% by required copper oxide catalyst. The monoethanolamine's (MEA) share equal to 12%, where ethanolamine, ethylene oxide and ammonia have shares of 54%, 26% and 20% respectively. Consequently, the optimization of processes related to ultrapure water, carbon capture and perhaps common application of catalyst's recycling would reduce related emissions. Taking into account the emissions related to wind energy the value for marine aquatic ecotoxicity category increased to 730 kg DCB-eq/kg Methanol, however the inclusion of credits for oxygen utilization at the WWTP could very significantly reduce the emissions. Furthermore, the high emissions related to methanol produced for biomass (950 kg DCB-eq/kg Methanol) are caused again by synthetic gas upstream chain (54%), methanol synthesis' electricity requirement (32%) and application of molybdenum (11%). The emissions related to methanol from natural gas are lower by over a half than of the biomass based methanol, whereas shares of natural gas upstream process, conditioning and application of molybdenum equal to 96% of related emissions (Fig. 14).

According to the ozone layer depletion impact category (Fig. 15), the emissions of methanol from natural gas is over 5 times higher than that of the biomass-based methanol and over 8 times higher
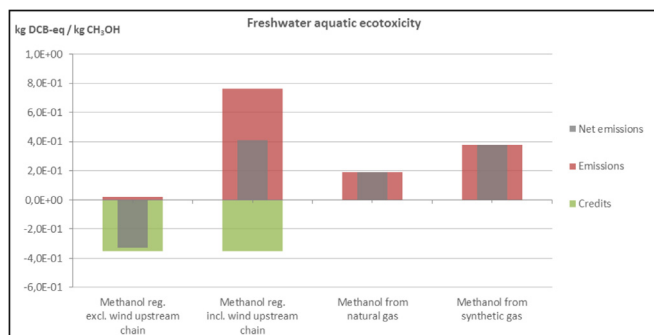

Fig. 11. Comparison of renewable methanol to conventional methanol in accordance to freshwater aquatic ecotoxicity.
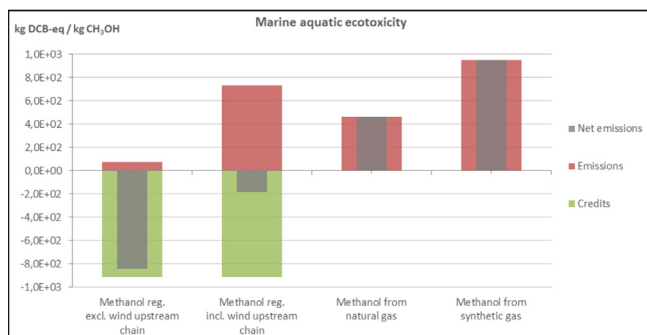

Fig. 13. Comparison of renewable methanol to conventional methanol in accordance to marine aquatic ecotoxicity.
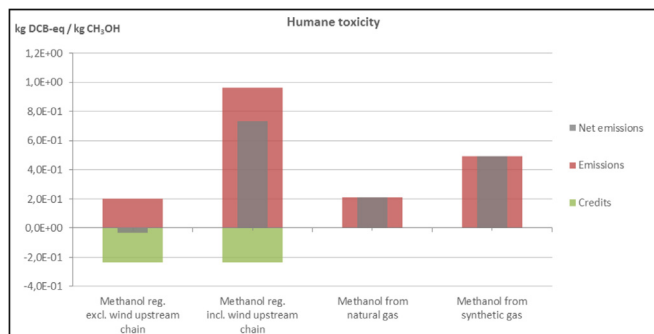

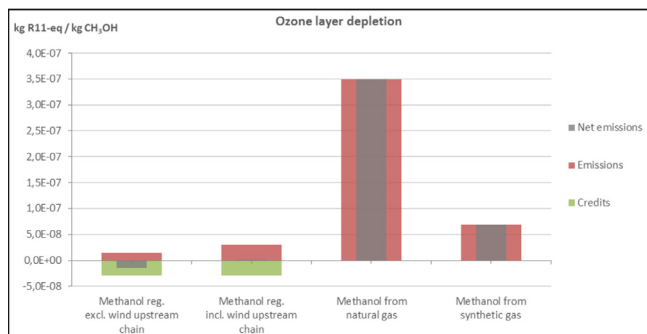**Fig. 12.** Comparison of renewable methanol to conventional methanol in accordance to humane toxicity.

Fig. 14. Comparison of renewable methanol to conventional methanol in accordance to ozone layer depletion.
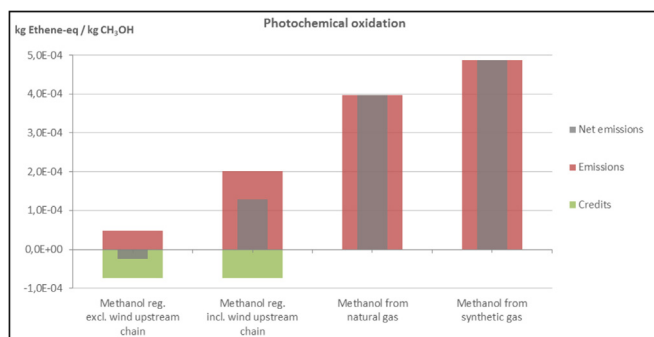
Fig. 15. Comparison of renewable methanol to conventional methanol in accordance photochemical oxidation.

than of renewable methanol with wind power upstream chain. The high result is in 89% caused by the natural gas upstream process and for the required heat is responsible for the 10%, obtained via combustion of the natural gas. Concerning the renewable methanol, the share of wind electricity upstream chain equals to 52% of the emissions and the share of application of ultrapure water for electrolysis is almost 44% of the emissions. After excluding the emissions related to wind electricity, the consumption of ultrapure water caused almost 92% of the emissions and almost 8% is an outcome of carbon capture method with MEA, whereas especially noticeable is ammonia requirement (56% of the MEA's impact).

The upstream chain of the ultrapure water required for the electrolysis process has the highest share (88%) in the emissions of renewable methanol following the photochemical oxidation impact category (Fig. 15). The carbon capture with primary amine (MEA) and copper oxide catalyst are responsible for 9.5% and 2.5% of the emissions respectively. The inclusion of wind electricity upstream chain increased 5 times the emissions related to renewable methanol, but due to different system boundaries are still lower than in the literature (Matzen und Demirel, 2016). Despite that, the emissions from re-MeOH with wind upstream process are still 2 times smaller than of the methanol from natural gas and almost 2.5 times smaller than the emissions of methanol from synthetic gas. For the higher emissions of ng-MeOH responsible are natural gas upstream process together with gas conditioning, methanol synthesis and utilized heat, which shares are 65.5%, 21.5% and 10% respectively. According to the photochemical oxidation impact category, 76% of the emissions from biomass based methanol are related to upstream chain of the synthetic gas, followed by methanol synthesis and its' electricity demand (22.5%).

According to the terrestrial ecotoxicity impact category (Fig. 16), the highest impact would be caused by the methanol from biomass
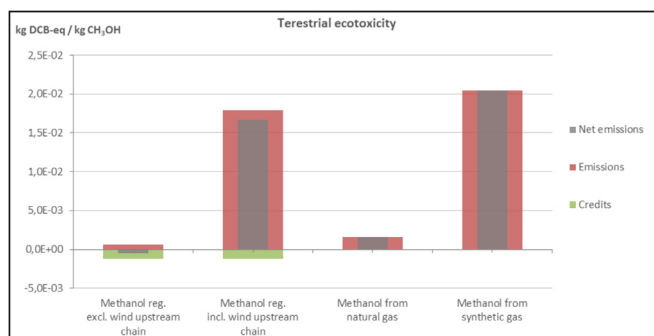
based synthetic gas. Here the synthetic gas upstream chain is responsible for almost 95.5% of the impact. Nevertheless, only $0.2e^{-02}$ kg DCB-eq/kg methanol reduction in emissions could be achieved by renewable methanol, from which 97% of the emissions would be caused by the wind electricity supply. Moreover, after excluding the wind electricity upstream chain a very significant reduction in emissions would be reached. The left emissions would be related to ultrapure water upstream chain (75%), chosen carbon capture (14.5%), and necessity of copper oxide catalyst (10%). On the other hand, emissions related to the natural gas based methanol were also estimated to be 12.5 times lower than of the biomass based methanol, by which resource upstream chain (69%), required heat for reforming (11%), electricity requirement for the methanol synthesis (9.5%), and application of the molybdenum (5%) are found to cause most of the emissions.

The final impact category was primary energy demand from non regenerative resources (Fig. 17). The natural gas upstream chain (87%) and heat requirement for the reforming (11%) play a significant role, thus utilizing the natural gas. For the biomass-based methanol a 3.8 times lower emission was forecasted, where again the synthetic gas upstream process has the highest share (71%) along with electricity demand for methanol synthesis (28%). Even lower impact on the environment according to this category would be caused by the renewable methanol (ultrapure water (27%) and MEA for carbon capture technique (6.5%) together with construction of windmills (66%), than of the biomass based methanol. The exclusion of wind upstream chain would increase the contribution of ultrapure water's utilization (79.5%) and MEA's application for carbon capture (20%) in the primary energy demand from non-renewable resources impact category.

Summarizing the production of renewable methanol with use of wind energy it would have lower impact on the environment according to 5 analysed categories (acidification potential, climate change, ozone layer depletion, photochemical oxidation, and primary energy demand from non-regenerative resources) than methanol from other sources. Additionally, according to eutrophication, marine aquatic ecotoxicity, and terrestrial ecotoxicity, the renewable methanol would cause lower emissions than biomass-based methanol. Taking into consideration the proposed utilization of the oxygen at the wastewater treatment plant (WWTP) and application of biogenic carbon dioxide from WWTP, then the renewable methanol with wind upstream chain would have lower emissions than other methanol processes according to 7 considered categories. However, even with application of another amine or another method for carbon dioxide capturing, according to 4 categories (depletion of abiotic resources, human toxicity, freshwater aquatic ecotoxicity, and terrestrial ecotoxicity) the renewable methanol with wind upstream chain would not reach lower
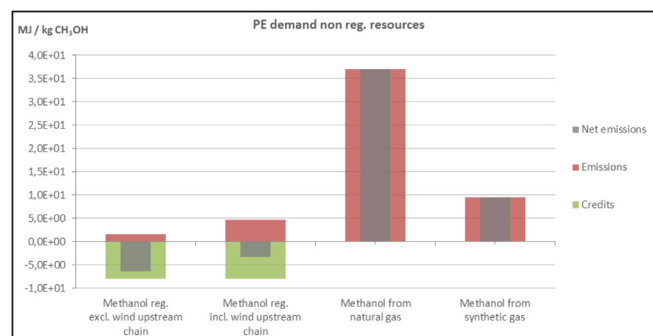

Fig. 16. Comparison of renewable methanol to conventional methanol in accordance terrestrial ecotoxicity.

Fig. 17. Comparison of renewable methanol to conventional methanol in accordance primary energy demand from non-renewable resources.

emissions as natural gas based or biomass based methanol.

As described in the introduction and chapter 2.6.5, due to the grid overloading, occasionally windmills or photovoltaic-plants in Germany need to be switch off (German Federal Association of Wind Energy, 2015). Therefore, assuming that the plans would not be used during the excess electricity production, the second renewable methanol scenario without wind upstream chain was evaluated. According to this scenario, the emissions related to all 11 evaluated impact categories are the lowest. Additionally, the calculated credits related to the application of the oxygen at the wastewater treatment plant and utilization of the biogenic CO_2, could completely reduce the negative impact on the environment according to 10 categories. However, this result was forecasted only for the methanol plant without wind upstream chain and under assumption that the aeration system at the WWTP could be flexible operated with oxygen.

3.2. By-products sensitivity analysis

Following the literature (Van-Dal und Bouallou, 2013), by-products like hydrocarbons, higher alcohols or methyl formate were not considered in simulation of the renewable methanol plant. However, they also stated that methyl formate could account for up to 0.4% of the produced methanol. Moreover, according to the conventional methanol production (Althaus et al., 2007), also formaldehyde would be present in the wastewater coming from the bottom of the distillation in amount of $0.1e^{-3}$ [kg/kg methanol]. Consequently it was decided to prepare a sensitivity analysis of the LCA where presence of formaldehyde and methyl formate would be considered in wastewater stream.

During the evaluation it was found out that both substances could release emissions related to 5 analysed impact categories: freshwater aquatic ecotoxicity, humane toxicity, marine aquatic ecotoxicity, photochemical oxidation, and terrestrial ecotoxicity. Consequently the LCA calculations were repeated for those 5 categories for renewable methanol with and without wind upstream chain. According to the results, although methyl formate would significantly increase emissions related to freshwater aquatic ecotoxicity (Fig. 18), but the other emissions would be very slightly impacted ($\leq 0.025\%$ of the total emissions) or would not increase the emissions related to photochemical oxidation. Despite the increase in emissions related to freshwater aquatic ecotoxicity, renewable methanol without wind upstream chain would deliver the lowest emission, even without assigned credits. Furthermore, the inclusion of wind upstream chain would still cause the highest emissions even after including the credits. On the other side, the presence of formaldehyde would very significantly increase emissions related to photochemical oxidation (Fig. 19), but instead would not increase other emissions. Despite the increased
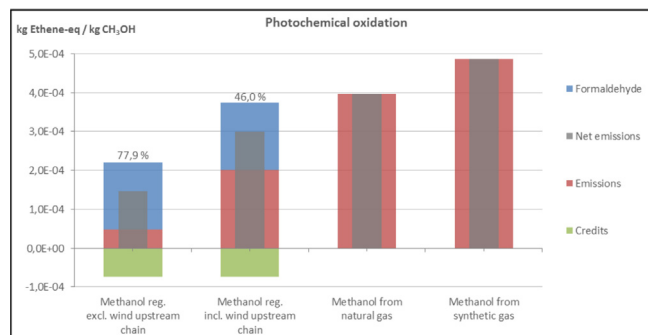

Fig. 19. Impact of the formaldehyde presence on the photochemical oxidation.

emissions related to photochemical oxidation, renewable methanol would still have lower impact on the environment than natural gas based or biomass based methanol.

4. Conclusions

This study presents a comparison of the emissions related to the natural gas based and biomass based, and renewable methanol. The renewable methanol is acquired from captured carbon dioxide from wastewater treatment plant and hydrogen produced from the excess of electricity. The methanol plant is theoretically located in Emden (North-West Germany) city, allowing application of the real, but city specific, data. According to the 11 impact categories, the production of methanol from the excess electricity, so without wind upstream chain, has a much lower impact on the environment. Furthermore, the utilization of oxygen at the wastewater treatment plant (WWTP) brought also significant credits, hence allowing reduction of electricity usage by the plant. Moreover, the concept of combining power-to-methanol plant with a WWTP has also an additional advantage in delivering sustainable carbon dioxide, which is not competing with food production and is also not dependent on the fossil fuel plants. However, the inclusion of emissions related wind electricity worsened significantly the results, hence renewable methanol could cause lower emissions according to 5 analysed categories (acidification potential, climate change, ozone layer depletion, photochemical oxidation, and primary energy demand from non-regenerative resources) out of 11. Moreover, because in the simulation by-products synthesis, like formaldehyde and methyl formate, was omitted, a sensitivity analysis was prepared. The results indicated that significant increase in emissions related to photochemical oxidation could be caused by the formaldehyde. The presence of methyl formate could significantly impact the environment according to freshwater aquatic ecotoxicity impact category. On the other side, via simulation and calculation it was shown that in a small city like Emden (North-West Germany) it is possible to convert the whole CO_2 available from local WWTP (required 2.86 GWh/a) via available excess of electricity (>5 GWh/a), hence already ensuring renewable methanol production for chemical industries or, due to lower toxicity (Olah et al., 2009), as an alternative fuel. However, in order to get even more meaningful results, the future research will concentrate on examination of the production effort for the plant components, because this could have a relatively big impact on the basis of the rather small sizing of the system. Additionally, the planned further extension of analysis into *Cradle-to-Grave* would support further evaluation of possible applications, via comparison of e.g. methanol fuel to other alternatives.
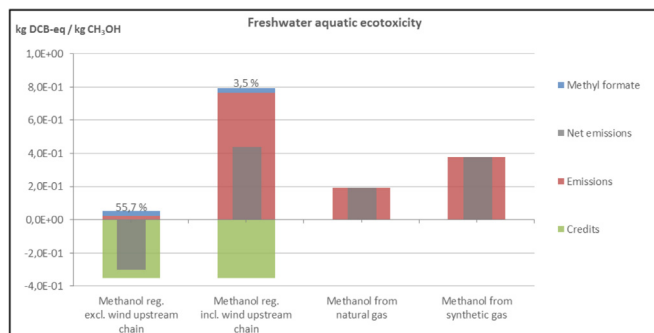

Fig. 18. Impact of the methyl formate presence on the freshwater aquatic ecotoxicity.

Funding

The project is carried out under the INTERREG Programme Germany Netherlands (INTERREG-Programm Deutschland-Niederland; #151074) and the 3.4 million € funding was received from the European Union, the Dutch Ministry of Economy (das niederländische Wirtschaftsministerium), MWEIMH NRW and the Lower Saxony State Chancellery (die Niedersächsische Staatskanzlei).

References

Abu-Zahra, Mohammad R.M., Schneiders, Léon H.J., Niederer, John P.M., Feron, Paul H.M., Versteeg, Geert F., 2007. CO2 capture from power plants. In: 8th International Conference on Greenhouse Gas Control Technologies, vol. 1(1), pp. 37–46. https://doi.org/10.1016/S1750-5836(06)00007-7.

Althaus, Hans Jörg, Hischier, Roland, Osses, Maggie, Primas, Alex, Hellweg, Stefanie, Jungbluth, Niels, Chudacoff, Mike, 2007. Life Cycle Inventories of Chemicals. Ecoinvent Report No. 8, v2.0. Swiss Centre for Life Cycle Inventories. EMPA Dübenauf. Online verfügbar unter. www.ecoinvent.org.

Anenberg, Susan C., Miller, Joshua, Minjares, Ray, Du, Li, Henze, Daven K., Lacey, Forrest, et al., 2017. Impacts and mitigation of excess diesel-related NOx emissions in 11 major vehicle markets. Nature 545 (7655), 467–471. https://doi.org/10.1038/nature22086.

Bicer, Yusuf, Dincer, Ibrahim, 2017a. Comparative life cycle assessment of hydrogen, methanol and electric vehicles from well to wheel. Int. J. Hydrogen Energy 42 (6), 3767–3777. https://doi.org/10.1016/j.ijhydene.2016.07.252.

Bicer, Yusuf, Dincer, Ibrahim, 2017b. Life cycle evaluation of hydrogen and other potential fuels for aircrafts. Int. J. Hydrogen Energy 42 (16), 10722–10738. https://doi.org/10.1016/j.ijhydene.2016.12.119.

Bourne, Simon, 25.04.2017. ITM Power 100MW Electrolyser. Hannover Messe: Hydrogen Fuel Cells Batteries; Group Exhibit. Technical Forum, Hannover.

Brynolf, Selma, Fridell, Erik, Andersson, Karin, 2014. Environmental assessment of marine fuels. Liquefied natural gas, liquefied biogas, methanol and bio-methanol. J. Clean. Prod. 74, 86–95. https://doi.org/10.1016/j.jclepro.2014.03.052.

Chemie.de Information Service GmbH, 2017. Methanol. Online verfügbar unter. http://www.chemie.de/lexikon/Methanol.html. zuletzt geprüft am 03.08.2017.

Cheng, Jay, 2009. Biomass to Renewable Energy Processes. Hg.. CRC Press.

Deublein, Dieter, Steinhauser, Angelika, 2011. Biogas from Waste and Renewable Resources. An Introduction, fourth ed. John Wiley & Sons, Hoboken.

Deutsche WindGuard GmbH, 2017. Status des Windenergieausbaus an Land in Deutschland. Wolfram, Axthelm. Online verfügbar unter. w.axthelm@wind-energie. https://www.wind-energie.de/system/files/attachments/press-release/2017/windenergie-land-analyse-deutscher-markt-2016-und-ausblick-2017-nach-gutem-ausbau-zahlen-fordernde/vdma-bwe-ausbau-wind-land-pk-2017-02-07-praesentation-final.pdf. zuletzt geprüft am 14.07.2017.

Dincer, I., Zamfirescu, C., 2016. A review of novel energy options for clean rail applications. J. Nat. Gas Sci. Eng. 28, 461–478. https://doi.org/10.1016/j.jngse.2015.12.007.

Dohmann, Max, Schröder, Markus, 2011. Energie in der Abwasserentsorgung. KA - Korrespondenz Abwasser, Abfall 6, 536–541. https://doi.org/10.3242/kae2011.06.001.

EN ISO 14040:2006, 07, 2006. Environmental Management — Life Cycle Assessment — Principles and Framework.

EN ISO 14044:2006, 07, 2006. Environmental Management — Life Cycle Assessment — Requirements and Guidelines.

German Federal Association of Wind Energy, 2015. Umschalten statt Abschalten - Impuls zur sinnvollen Erschließung der Bereiche Mobilität und Wärme mit Erneuerbarer Energie. Bundesverband WindEnergie. Online verfügbar unter. https://www.wind-energie.de/presse/pressemitteilungen/2015/umschalten-statt-abschalten-impuls-zur-sinnvollen-erschliessung-der. zuletzt aktualisiert am 11.09.2015, zuletzt geprüft am 14.07.2017.

Hao, Han, Liu, Zongwei, Zhao, Fuquan, Du, Jiuyu, Chen, Yisong, 2017. Coal-derived alternative fuels for vehicle use in China. A review. J. Clean. Prod. 141, 774–790. https://doi.org/10.1016/j.jclepro.2016.09.137.

Hoppe, Wieland, Bringezu, Stefan, 2016. Vergleichende Ökobilanz der CO2-basierten und konventionellen Methan- und Methanolproduktion. uwf 24 (1), 43–47. https://doi.org/10.1007/s00550-016-0389-4.

Hoppe, Wieland, Thonemann, Nils, Bringezu, Stefan, 2017. Life cycle assessment of carbon dioxide-based production of methane and methanol and derived polymers. J. Ind. Ecol. 7 (3), 181. https://doi.org/10.1111/jiec.12583.

IHS Markit, 2017. 2014 World Methanol Consumption. Online verfügbar unter. https://www.ihs.com/products/chemical-market-methanol-global.html. zuletzt geprüft am 01.08.2017.

ISPT, 2017. Power to Ammonia. Feasibility Study for the Value Chains and Business Cases to Produce CO2- Free Ammonia Suitable for Various Market Applications. Institute for Sustainable Process Technology. Online verfügbar unter. http://www.ispt.eu/power-ammonia-renewable-energy-co2-free-ammonia-chemical-feedstock-fuel/. zuletzt geprüft am 14.07.2017.

Jadhav, Suhas G., Vaidya, Prakash D., Bhanage, Bhalchandra M., Joshi, Jyeshtharaj B., 2014. Catalytic carbon dioxide hydrogenation to methanol: a review of recent

studies. Chem. Eng. Res. Des. 92 (11), 2557–2567. https://doi.org/10.1016/j.cherd.2014.03.005.

Jungbluth, Niels, Emmenegger, Mireille Faist, Dinkel, Fredy, Settler, Cornelia, Doka, Gabor, Chudacoff, Mike, et al., 2007. Life Cycle Inventories of Bioenergy. ecoinvent report No. 17. Swiss Centre for Life Cycle Inventories, Dübendorf. Online verfügbar unter. www.ecoinvent.org.

Kemp, Ian, 2007. Pinch Analysis and Process Integration. Elsevier Ltd., Oxford UK.

Koornneef, Joris, van Keulen, Tim, Faaij, André, Turkenburg, Wim, 2008. Life cycle assessment of a pulverized coal power plant with post-combustion capture, transport and storage of CO2. In: TCCS-4: The 4th Trondheim Conference on CO2 Capture, Transport and Storage 2(4), pp. 448–467. https://doi.org/10.1016/j.ijggc.2008.06.008.

Lenntech, B.V., 2017. Belüftung von Abwasser. Die Turbinenbelüftung versorgt Abwasser und Kanalwasser mit Sauerstoff. Online verfügbar unter. http://www.lenntech.de/beluftung-abwasser.htm. zuletzt geprüft am 20.07.2017.

Li, Zheng, Gao, Dan, Chang, Le, Liu, Pei, Pistikopoulos, Efstratios N., 2010. Coal-derived methanol for hydrogen vehicles in China. Energy, environment, and economic analysis for distributed reforming. Chem. Eng. Res. Des. 88 (1), 73–80. https://doi.org/10.1016/j.cherd.2009.07.003.

Lindenthal, Wolfgang, Uhlenhut, Frank, Steinigeweg, Sven, Borchert, Axel, 2013. Das gekoppelte system Abwasserreinigung/Klärschlammfaulung. gwf-Wasser/Abwasser 09, 988–994. Online verfügbar unter. https://www.gwf-gas.de/produkte/2013-das-gekoppelte-system-abwasserreinigungklaerschlammfaulung/.

Matzen, Michael, Demirel, Yaşar, 2016. Methanol and dimethyl ether from renewable hydrogen and carbon dioxide. Alternative fuels production and life-cycle assessment. J. Clean. Prod. 139, 1068–1077. https://doi.org/10.1016/j.jclepro.2016.08.163.

Methanol Institute, 2017. Uses of Methanol. Chemical/Energy/Wastewater Treatment. Online verfügbar unter. http://www.methanol.org/uses/. zuletzt geprüft am 01.08.2017.

Mignard, Dimitri, Pritchard, Colin, 2008. On the use of electrolytic hydrogen from variable renewable energies for the enhanced conversion of biomass to fuels. Chem. Eng. Res. Des. 86 (5), 473–487. https://doi.org/10.1016/j.cherd.2007.12.008.

Moret, Séverine, Dyson, Paul J., Laurenczy, Gábor, 2014. Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media. Nat. Commun. 5, 4017. https://doi.org/10.1038/ncomms5017.

Neslen, Arthur, 2015. Wind Power Generates 140% of Denmark's Electricity Demand. The Guardian. Online verfügbar unter. https://www.theguardian.com/environment/2015/jul/10/denmark-wind-windfarm-power-exceed-electricity-demand. zuletzt aktualisiert am 10.07.2015, zuletzt geprüft am 19.07.2017.

Olah, George A., Goeppert, Alain, Prakash, G. K. Surya, 2009. Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. J. Org. Chem. 74 (2), 487–498. https://doi.org/10.1021/jo801260f.

Pérez-Fortes, Mar, Schöneberger, Jan C., Boulamanti, Aikaterini, Tzimas, Evangelos, 2016. Methanol synthesis using captured CO2 as raw material: techno-economic and environmental assessment. Appl. Energy 161, 718–732. https://doi.org/10.1016/j.apenergy.2015.07.067.

PLANET- Planungsgruppe Energie und Technik GbR, 2013. Liquid Hydrogen Outline. IDEALHY Project. Online verfügbar unter. http://www.idealhy.eu/index.php?page=lh2_outline. zuletzt geprüft am 03.08.2017.

Rochelle, Gary T., 2009. Amine scrubbing for CO2 capture. Science (New York, N.Y.) 325 (5948), 1652–1654. https://doi.org/10.1126/science.1176731.

Sahki, Rachid, Benlounes, Ouarda, Chérifi, Ouiza, Thouvenot, René, Bettahar, Mohammed M., Hocine, Smain, 2011. Effect of pressure on the mechanisms of the CO2/H2 reaction on a CO-precipitated CuO/ZnO/Al2O3 catalyst. React. Kinet. Mech. Catal. 103 (2), 391–403. https://doi.org/10.1007/s11144-011-0311-6.

Shen, Wei, Han, Weijian, Chock, David, Chai, Qinhu, Zhang, Aling, 2012. Well-to-wheels life-cycle analysis of alternative fuels and vehicle technologies in China. Energy Policy 49, 296–307. https://doi.org/10.1016/j.enpol.2012.06.038.

Stadtwerke Emden, 2016. Energiestrukturdaten (VNB). Online verfügbar unter. https://stadtwerke-emden.de/netz/veroeffentlichungspflichten/.

Sternberg, André, Bardow, André, 2015. Power-to-What? — Environmental assessment of energy storage systems. Energy Environ. Sci. 8 (2), 389–400. https://doi.org/10.1039/C4EE03051F.

Strazza, C., Del Borghi, A., Costamagna, P., Traverso, A., Santin, M., 2010. Comparative LCA of methanol-fuelled SOFCs as auxiliary power systems on-board ships. Appl. Energy 87 (5), 1670–1678. https://doi.org/10.1016/j.apenergy.2009.10.012.

The Guardian, 2016. Scotland's Wind Turbines Covers All its Electricity Needs for a Day. Online verfügbar unter. https://www.theguardian.com/environment/2016/aug/11/scotland-completely-powered-by-wind-turbines-for-a-day. zuletzt aktualisiert am 11.08.2016, zuletzt geprüft am 19.07.2017.

Trudewind, Clemens A., Schreiber, Andrea, Haumann, David, 2014a. Photocatalytic methanol and methane production using captured CO2 from coal power plants. Part II — well-to-Wheel analysis on fuels for passenger transportation services. J. Clean. Prod. 70, 38–49. https://doi.org/10.1016/j.jclepro.2014.02.024.

Trudewind, Clemens A., Schreiber, Andrea, Haumann, David, 2014b. Photocatalytic methanol and methane production using captured CO2 from coal-fired power plants. Part I — a Life Cycle Assessment. J. Clean. Prod. 70, 27–37. https://doi.org/10.1016/j.jclepro.2014.02.014.

Uusitalo, Ville, Väisänen, Sanni, Inkeri, Eero, Soukka, Risto, 2017. Potential for greenhouse gas emission reductions using surplus electricity in hydrogen,

methane and methanol production via electrolysis. Energy Convers. Manag. 134, 125–134. https://doi.org/10.1016/j.enconman.2016.12.031.

Van-Dal, Éverton Simões, Bouallou, Chakib, 2013. Design and simulation of a methanol production plant from CO2 hydrogenation. J. Clean. Prod. 57, 38–45. https://doi.org/10.1016/j.jclepro.2013.06.008.

Vanden Bussche, K.M., Froment, G.F., 1996. A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/ Al2O3Catalyst. J. Catal. 161 (1), 1–10. https://doi.org/10.1006/jcat.1996.0156.

WeltN24 GmbH, 2016. Warum es am Muttertag einen Ökostrom-Rekord gab. Online verfügbar unter. https://www.welt.de/155254599. zuletzt aktualisiert am 11.05.2016, zuletzt geprüft am 14.07.2017.

Zhen, Xudong, Wang, Yang, 2015. An overview of methanol as an internal combustion engine fuel. Renew. Sustain. Energy Rev. 52, 477–493. https://doi.org/10.1016/j.rser.2015.07.083.